chem 5390

Advanced X-ray Analysis

LECTURE 11

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Diffraction Theory

Diffraction Methods

Powder Method

For powders, the crystal is reduced to a very fine powder or microscopic grains.

The sample, in a holder, is placed in a beam of monochromatic x-rays.

Each particle is a tiny crystal, oriented at random with respect to the incident beam. By chance each plane is represented or oriented correctly to diffract at a set θ.

Diffraction Theory

Diffraction Methods

Powder Method

The entire mass of the powder is equivalent to a single crystal rotated, not about one axis, but about all possible axes.

This method is good for determining lattice parameters with high precision and for the identification of phases.

Diffraction Theory

Crystal Structure Determination

Crystal structure of a substance determines the diffraction pattern of that substance.

Diffraction Theory

Crystal Structure Determination

The shape and size of the unit cell determines the angular positions of the diffraction lines and the arrangement of the atoms within the unit cell determines the relative intensities of the lines.

Crystal structure	Diffraction pattern
Unit cell	Line positions
Atom positions	Line intensities

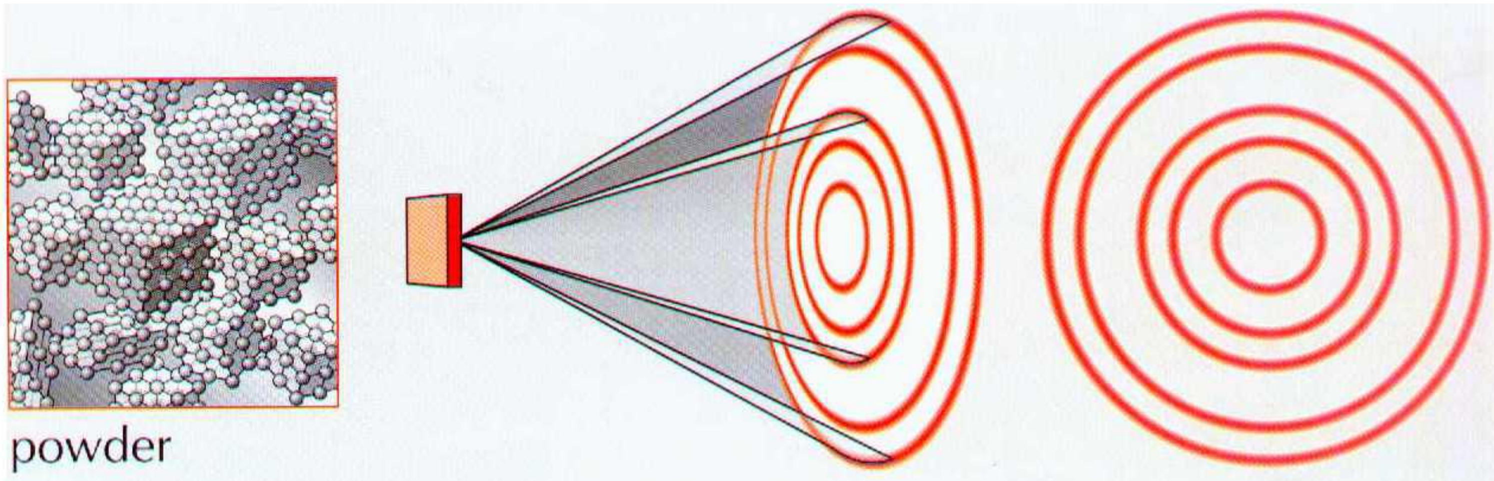
Diffraction Theory

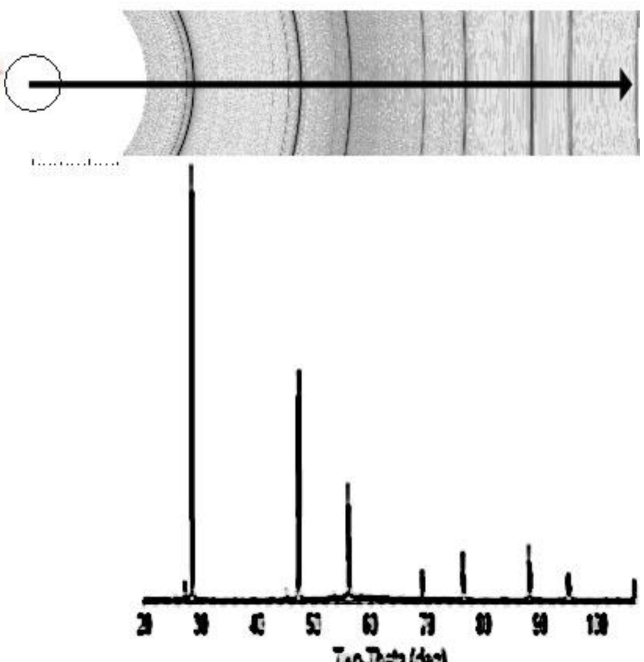
Crystal Structure Determination

- When a completely randomized powder sample is placed into an X-ray beam the result is a complete Debye cone. When analyzing this type of sample any linear scan through the Debye cones will give an accurate powder pattern. This "linear scan" is exactly how a conventional Bragg-Brentano powder diffraction system works.

Diffraction Theory

Powder Diffraction





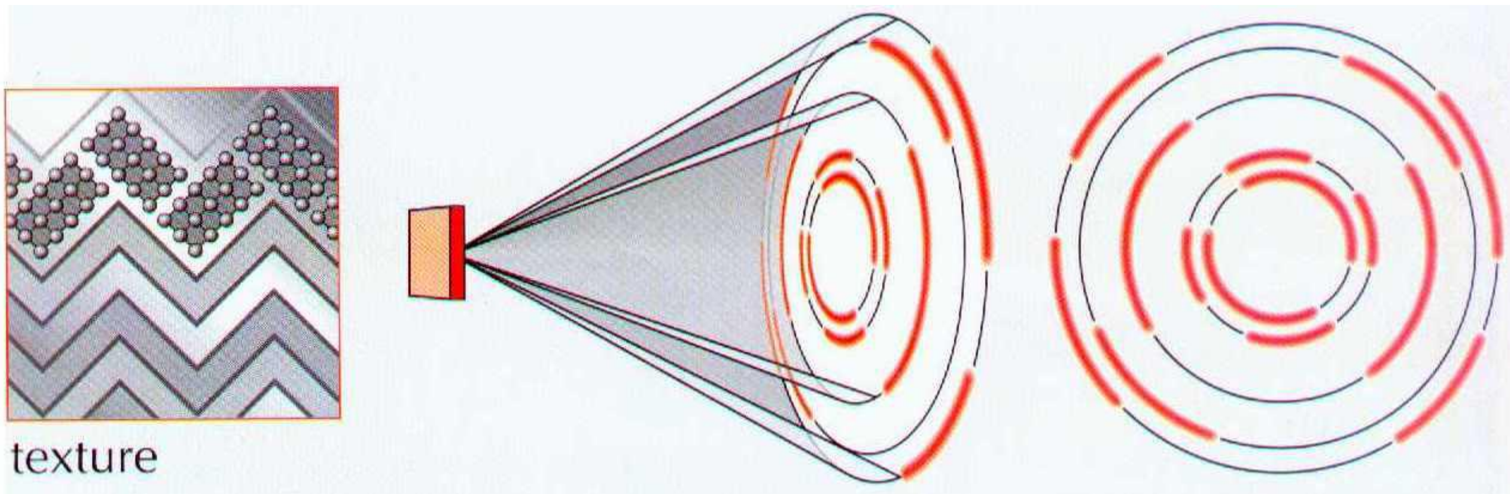
Diffraction Theory

Crystal Structure Determination

- However, when a system is not a completely randomized powder (texture measurement) or if there is only one or just a few crystal (microdiffraction measurement) or a combination of both, the result is an incomplete Debye cone.

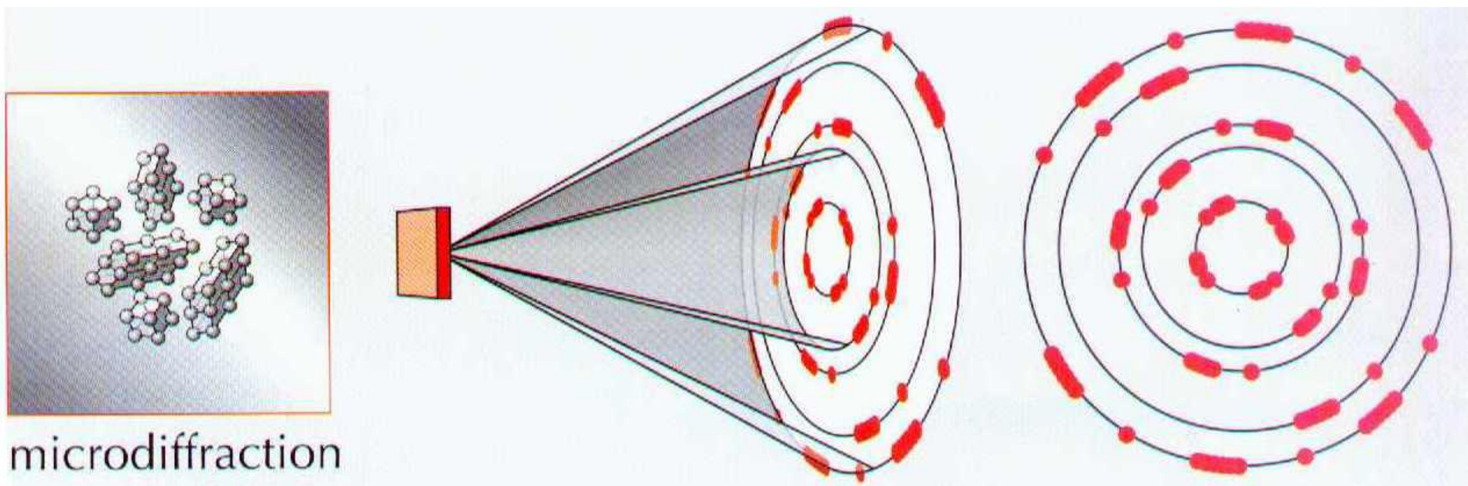
Diffraction Theory

Powder Texture



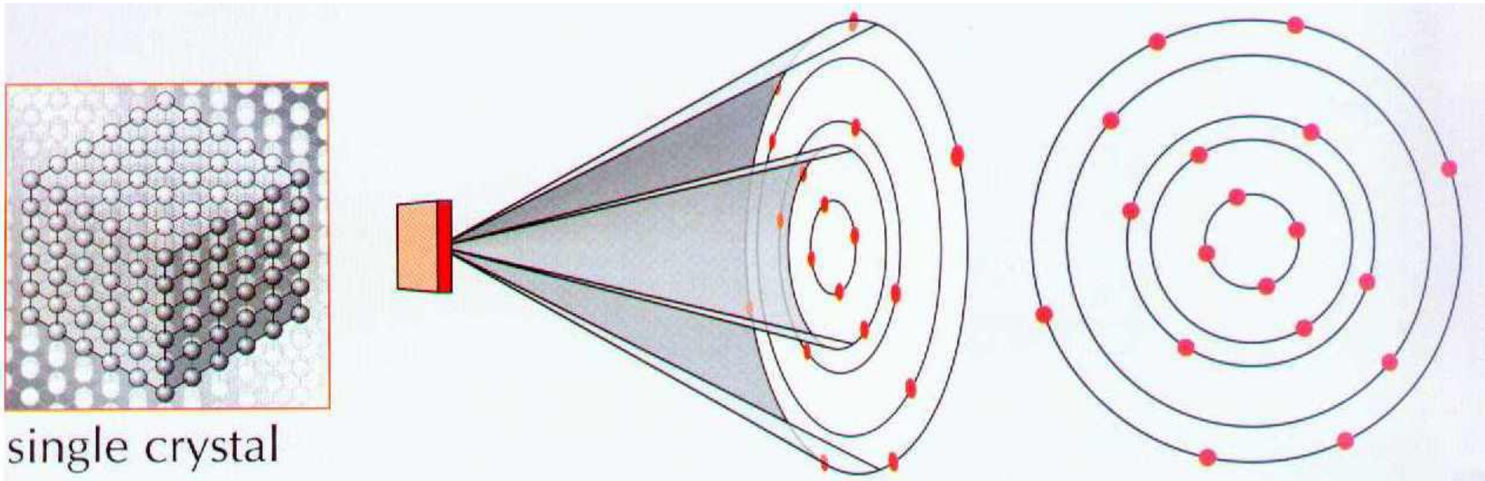
Diffraction Theory

Microdiffraction



Diffraction Theory

Single Crystal



Diffraction Theory

Diffraction Methods

Diffraction occurs when $\lambda = 2\,d \sin\theta$ is satisfied, putting stringent conditions on λ and θ for any given crystal.

To find the diffracted beams, either λ or θ must be varied experimentally.

Diffraction Theory

Diffraction Methods

Method	λ	θ
Laue	Variable	Fixed
Rotating-crystal	Fixed	Variable (in part)
Powder	Fixed	Variable

Diffraction Theory

Diffraction Methods

1. Laue Camera: With a polychromatic incident beam many planes will meet the Bragg condition and tracing the 2-d pattern on a photographic film will reveal the planes of a zone.

2. Rotating Crystal Method: For a monochromatic beam and a single crystal. Rotate the crystal during diffraction experiment to bring Bragg planes into alignment.

3. Powder Method: Monochromatic beam, polycrystalline sample. Usually done with a flat film in pinhole arrangement.

4. Diffractometer Method: Similar to the powder method but uses a step-scanner and a line beam. Usually involves a polycrystalline sample.

Diffraction Theory

Diffraction Methods

1. Laue Method

First diffraction method used.

Beam of white radiation (continuous spectrum) from an x-ray tube falls on a fixed single crystal.

The Bragg angle, θ, is fixed for every set of planes in the crystal.

The set of planes selects and diffracts that λ which will satisfy Braggs's law for d and θ.

Each diffracted beam has a different λ.

Diffraction Theory

Diffraction Methods

1. **Laue Method**

Laue can be transmission or back-reflecting mode

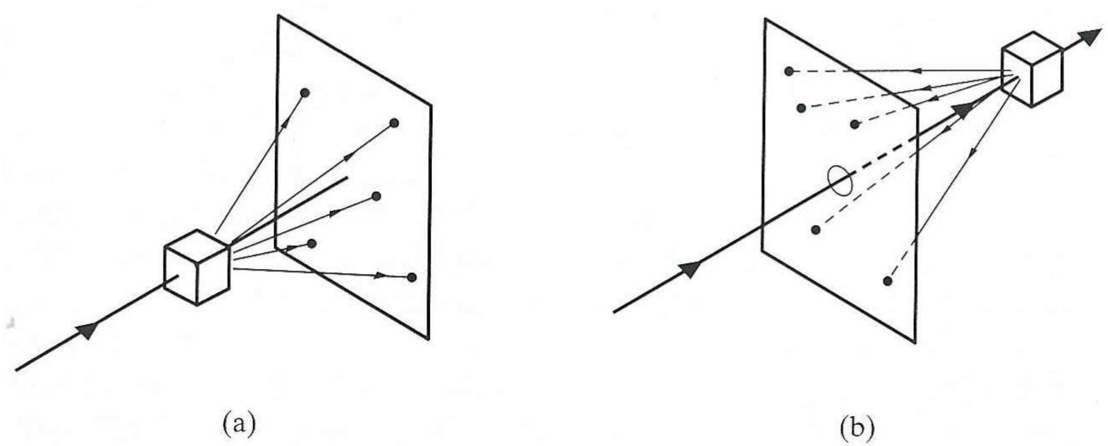


Figure 3-9 (a) Transmission and (b) back-reflection Laue methods.

Diffraction Theory

Diffraction Methods

1. Laue Method

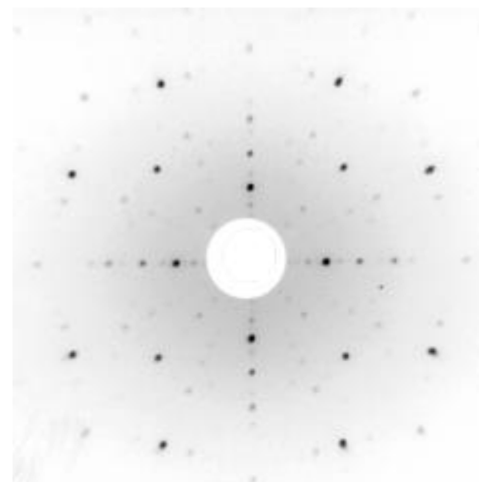
The diffracted beam forms an array of spots called a spot pattern.

These spots become distorted or smeared if the crystal is bent or twisted.

So the main use for Laue is determination of crystal orientation and assessment of crystal quality.

Diffraction Theory

Laue



Diffraction Theory

Diffraction Methods

2. Rotating Crystal Method

A single crystal is mounted with one of its axis normal to a monochromatic x-ray beam.

In the past, a cylindrical film surrounds the crystal which is rotated about a chosen direction.

Method used to determine unknown crystal structure.

Diffraction Theory

Diffraction Methods

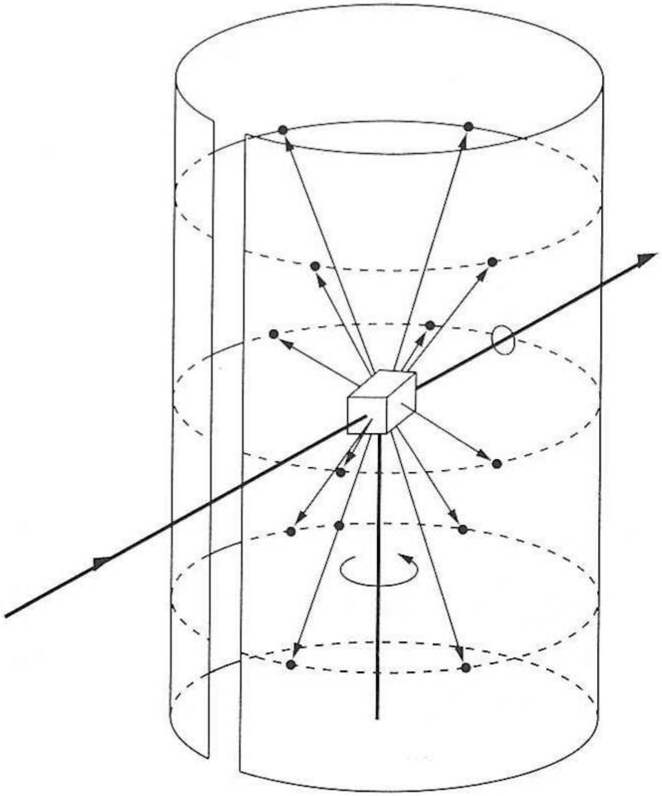


Figure 3-14 Rotating-crystal method.

Diffraction Theory

Diffraction Methods

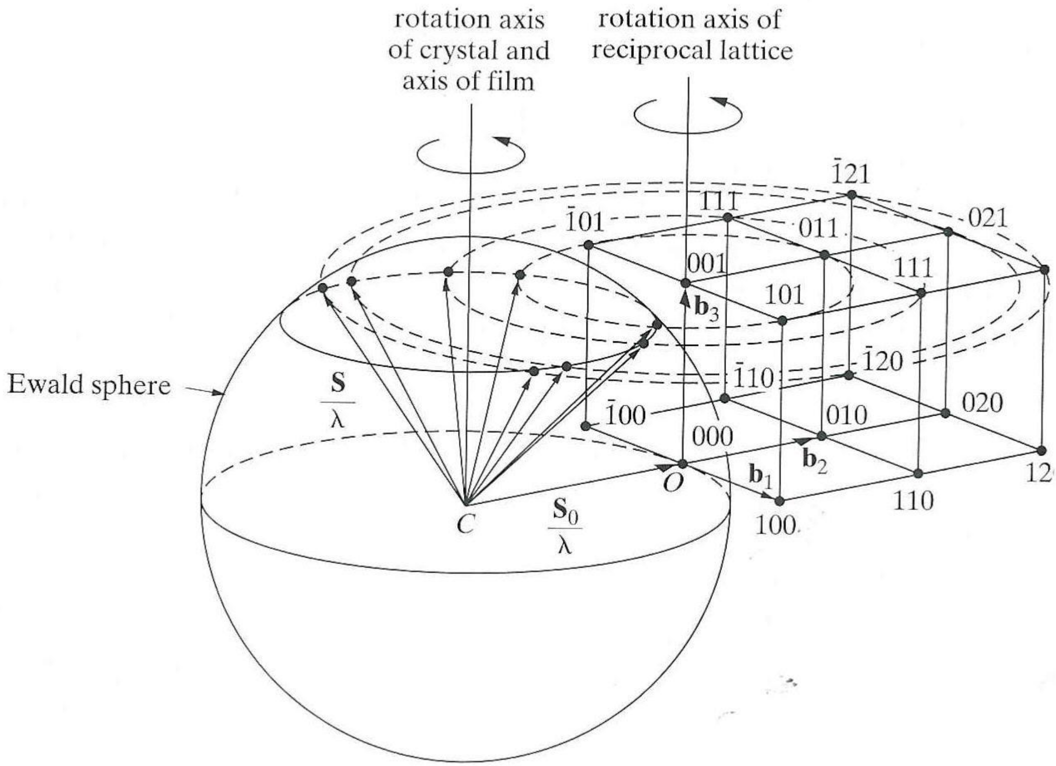


Figure 3-16 Reciprocal-lattice treatment of rotating-crystal method.

Diffraction Theory

Diffraction Methods

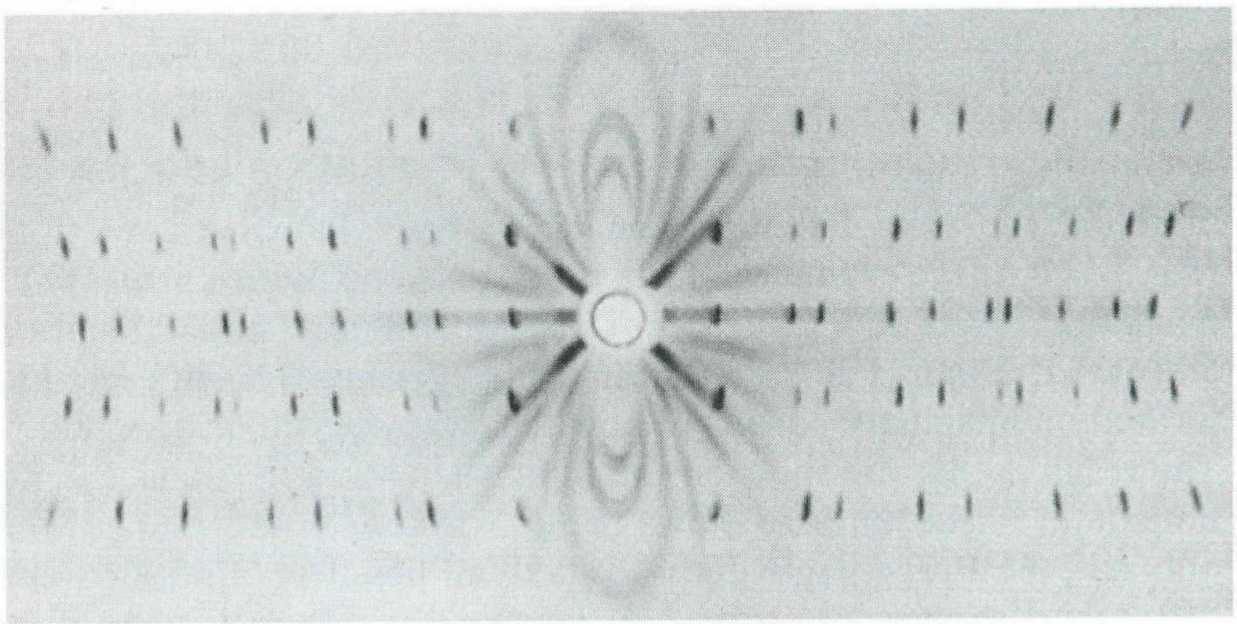
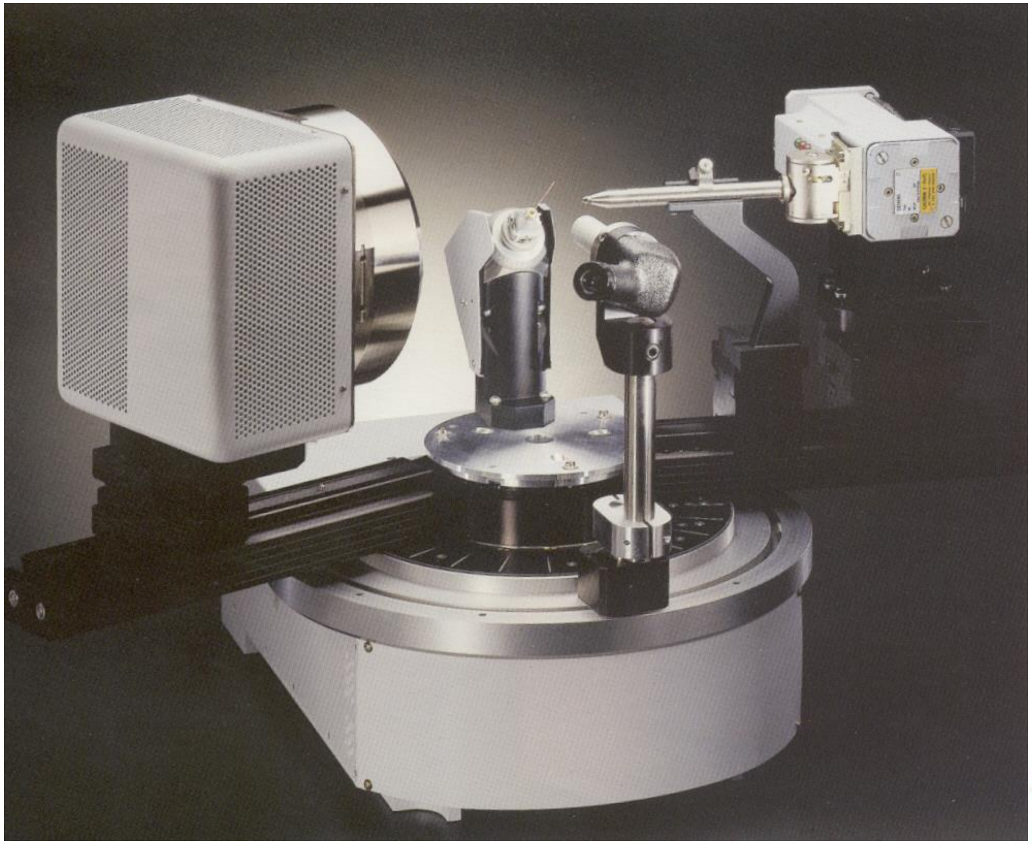


Figure 3-15 Rotating-crystal pattern of a quartz crystal (hexagonal) rotated about its c axis. Filtered copper radiation. (The streaks are due to the white radiation not removed by the filter.) (Courtesy of B. E. Warren.)

Diffraction Theory

Diffraction Methods

2. Rotating Crystal Method



Diffraction Theory

Diffraction Methods

2. Single-crystal

Use four – circle diffractometer to give an additional degree of freedom.

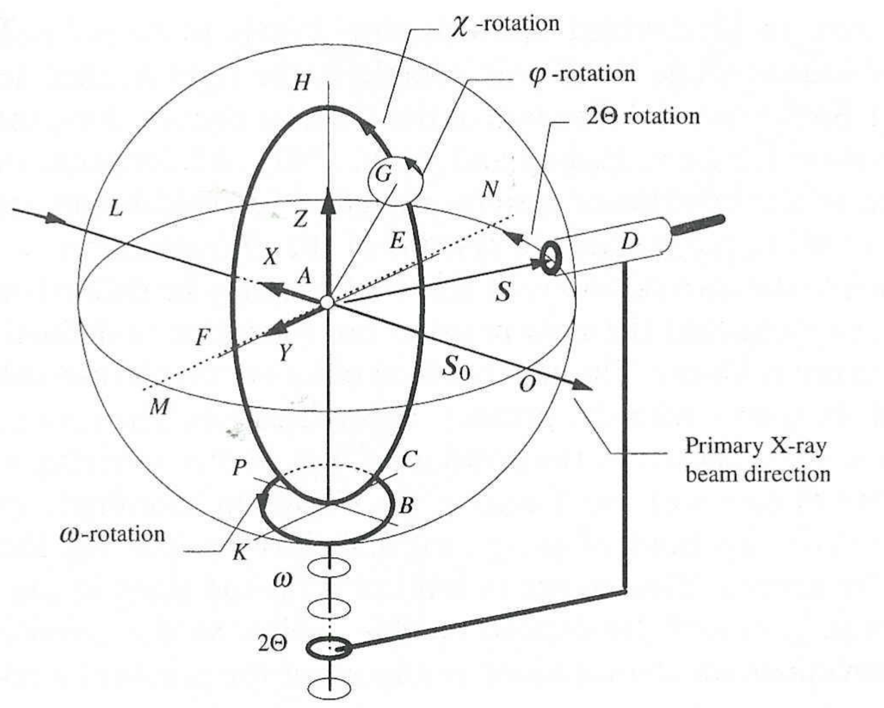


Fig. 2.11. Geometry principle of four-circle equatorial diffractometer.

Diffraction Theory

Diffraction Methods

2. Single-crystal

X-ray beam is fixed.

Detector rotates

Axes are φ, ω, χ, 2θ (phi, omega, chi, 2-theta)

Mechanical systems for sample orientation includes:

-sample holder

-goniometer head (provides sample 3 translations to set crystal in center.

All parts of goniometer have to be rigid and backlash free.

Diffraction Theory

Diffraction Methods

2. Single-crystal

Goniometer arrangements include:

-symmetric – eulerian cradle

-asymmetric

-Kappa, κ

Kappa – χ is replaced with κ-axis inclined to the vertical axis of the diffractometer.

Diminishes observation to detector .

Diffraction Theory

Diffraction Methods

2. Single-crystal

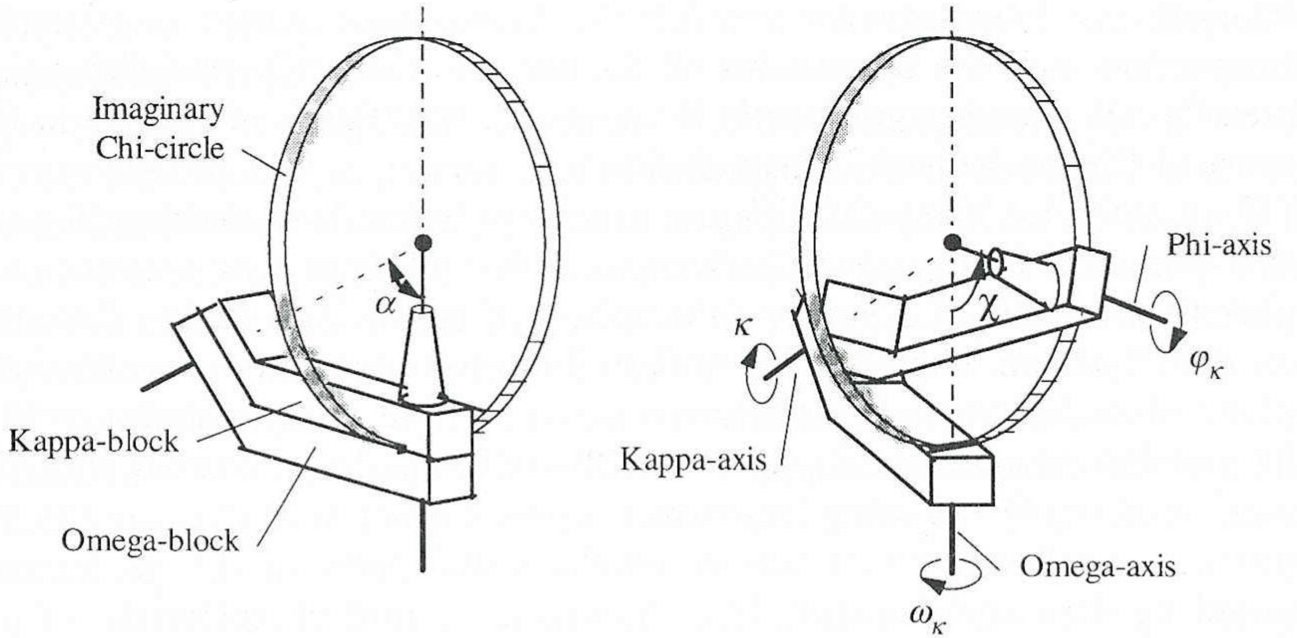


Fig. 3.21. Geometry principle of CAD4 κ-goniometer compared with the 'classical' four-circle diffractometer.

Diffraction Theory

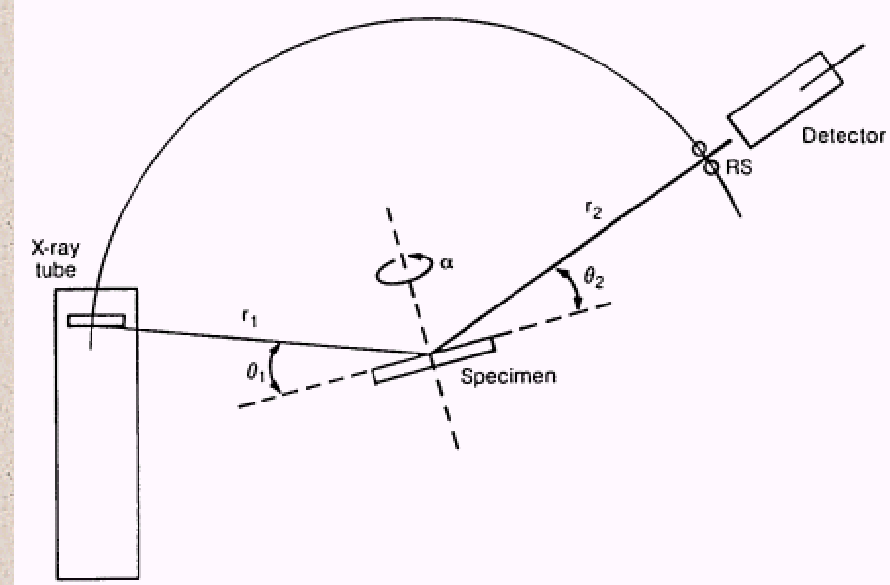
Diffraction Methods

3. Diffractometer (Powder) Method

Diffraction Theory

X-ray Diffraction – The diffractometer

Common mechanical movements in powder diffractometers



Type	Tube	Specimen	Receiving Slit	r_1	r_2
Bragg-Brentano $\theta:2\theta$	Fixed	Varies as θ *	Varies as 2θ	Fixed	$= r_1$
Bragg-Brentano $\theta:\theta$	Varies as θ	Fixed *	Varies as θ	Fixed	$= r_1$
Seeman-Bohlin	Fixed	Fixed *	Varies as 2θ	Fixed	Variable
Texture Sensitive (Ladell)	Fixed	Varies as θ precesses about α	Varies as 2θ	Fixed	Variable

*Generally fixed, but can rotate about α or rock about goniometer axis.

Diffraction Theory

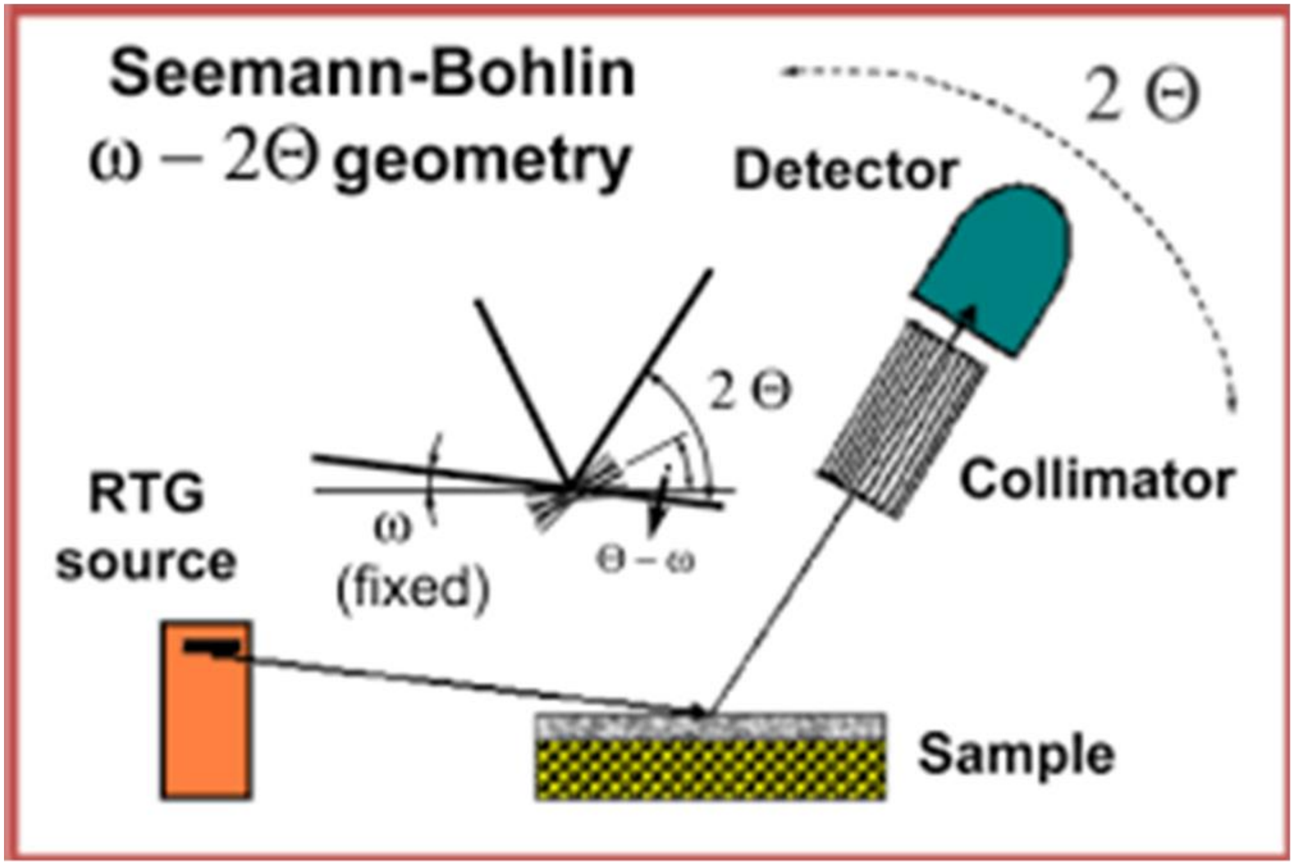
Diffraction Methods

Seemann-Bohlin:

- this method is suitable for stress measurement
- for low angle of incidence, the penetration depth does not vary much with the diffraction angle but it is strongly dependent on the angle of incidence
- due to the focusing geometry, the diffraction intensities are relatively high
- as the penetration depth is rather low (that is approximately ten times less than in the Bragg--Brentano method), the technique is especially suitable for thin films

Diffraction Theory

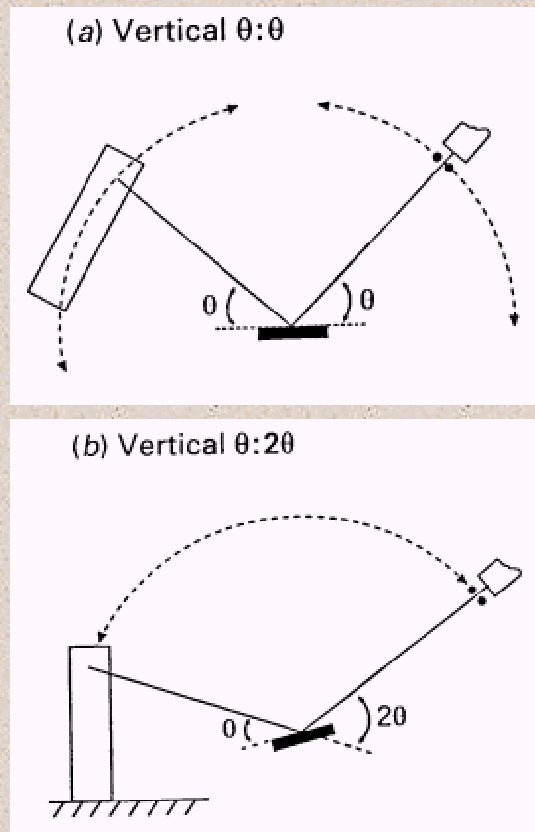
Diffraction Methods

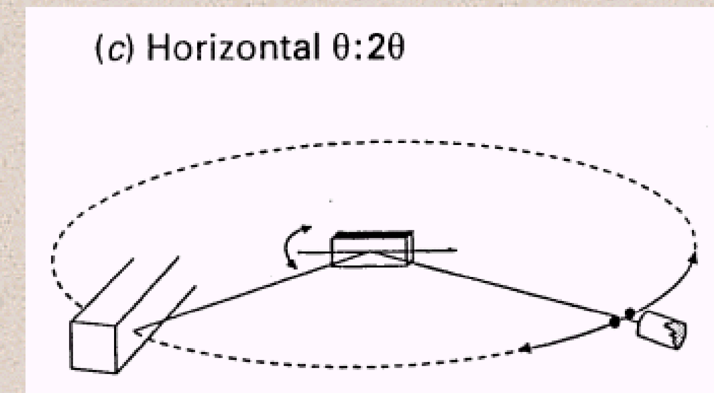


Diffraction Theory

X-ray Diffraction – The diffractometer

- **The Bragg-Brentano diffractometer**





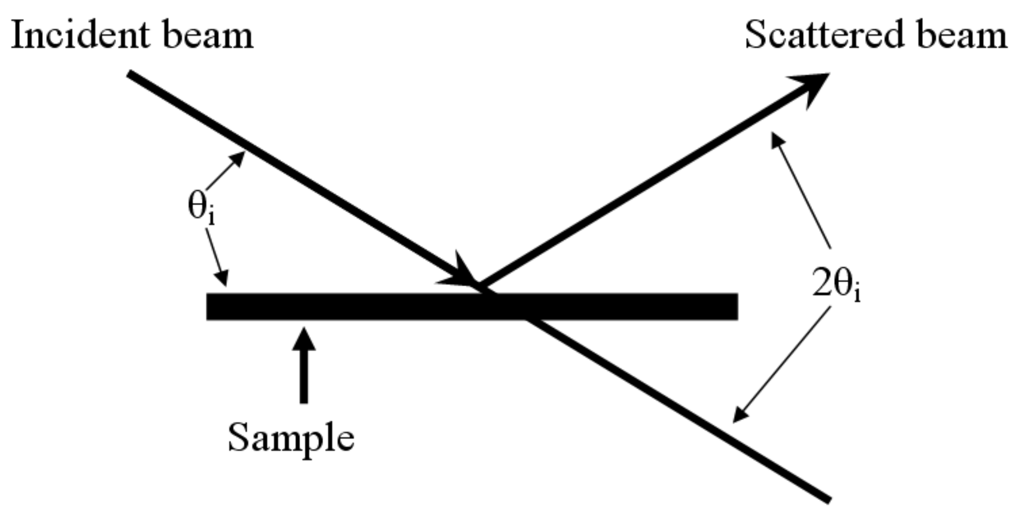
Various configurations of the Bragg-Brentano parafocusing diffractomenter

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

The θ - 2θ scan maintains these angles with the sample, detector and X-ray source.



Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

The θ - 2θ scan maintains these angles with the sample, detector and X-ray source.

The incident X-rays may reflect in many directions but will only be measured at one location so we will require that:

Angle of incidence (θ_i) = Angle of reflection (θ_r)

This is done by moving the detector twice as fast in θ as the source. So, only where $\theta_i = \theta_r$ is the intensity of the reflect wave (counts of photons) measured.

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- Phase Analysis
- Texture Analysis
- Lattice Parameters
- Crystallite Size
- Stress Analysis
- Strain Analysis

Diffraction Theory

Reading Assignment:

Read Chapter 3 from textbooks:

-Introduction to X-ray powder
Diffractometry by Jenkins and Synder

-Elements of X-ray Diffraction by
Cullity and Stock

Read Chapter 4 from textbook:

-Elements of X-ray Diffraction by
Cullity and Stock

Read Chapter 8 from:
-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 13 from:
-Elements of X-ray Diffraction, 3rd edition, by Cullity and Stock

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